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Mg assisted flux growth and characterization of single crystalline Sm2Co17

Tej Nath Lamichhane
Iowa State University and Ames Laboratory, tejl@iastate.edu

Qisheng Lin
Iowa State University and Ames Laboratory, qslin@ameslab.gov

Valentin Taufour
Iowa State University and Ames Laboratory

Andriy Palasyuk
Ames Laboratory, palasyuk@ameslab.gov

Tribhuwan Pandey
Oak Ridge National Laboratory

See next page for additional authors

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Abstract
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Authors
Tej Nath Lamichhane, Qisheng Lin, Valentin Taufour, Andriy Palasyuk, Tribhuwan Pandey, David Parker, Sergey L. Bud'ko, and Paul C. Canfield

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Tej Nath Lamichhane,[1,2,a)] Qisheng Lin,[1] Valentin Taufour,[1,3] Andriy Palasyuk,[1] Tribhuwan Pandey,[4] David Parker,[4] Sergey L. Bud'ko,[1,2] and Paul C. Canfield[1,2]

AFFILIATIONS

[1]Ames Laboratory, Iowa State University, Ames, Iowa 50011, U.S.A.
[2]Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, U.S.A.
[3]Department of Physics, University of California Davis, Davis, California 95616, U.S.A.
[4]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

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[a)]**Electronic mail: Corresponding:** tejl@iastate.edu

ABSTRACT

This paper presents details of Mg-assisted flux growth of Sm_2Co_{17} single crystals in a Ta crucible well below the melting temperature of binary Sm_2Co_{17}. Both the crushed single crystalline powder x-ray diffraction (XRD) and single crystalline XRD data revealed the Th_2Zn_{17} type rhombohedral(R-3m) crystal structure. Ta atom is found to be statistically replacing the Co-Co dumbbell with its position being at the center of the dumbbell. The Curie temperature of our lightly Mg and Ta doped Sm_2Co_{17} sample is determined to be ~1100 K using method of generalized Bloch law fitting of easy axis spontaneous magnetization data.

I. INTRODUCTION

Despite of the wide application of Sm_2Co_{17} as a high performance magnet, its basic physical properties are not as extensively studied as other high flux commercial permanent magnets such as $Nd_2Fe_{14}B$, $SmCo_5$, probably due to the lack of easily accessible single crystalline sample. Various physical properties of single crystalline $Nd_2Fe_{14}B$ sample are studied on self flux grown sample.[1–3] In case of $SmCo_5$ and other high cobalt content binary R-Co compounds single crystals, the traditional self-flux growth technique out of binary melt is not readily accomplished. Most of the Sm-Co binary compounds are highly reactive with traditional ceramics crucibles and mostly peritectic with very high exposed liquidus temperature (>1300 °C). Single crystal growth by zone melting, Bridgman and Czochralski technique are also difficult because of high reactivity of Sm-Co compounds and high vapour pressure of Sm. The quality of Bridgman technique grown crystals strongly depend on the quality and type of the crystal growth crucibles and also needs an excess amount of Sm. The Bridgman technique for $SmCo_5$ growth was successful only using the Ta crucible.[4] For Sm_2Co_{17}, the pyrolitic sintered BN-crucible could not assist crystal growth. Additionally, the BN-coated recrystallized $A1_2O_3$ crucible also produced a reacted complex layer containing Al, B, N and R when reached up to 1400 °C during the Bridgman crystal growth technique.[5] In this work we use Mg-flux to reduce the melting temperature and allow for the use of a sealed Ta crucible to hold the melt to get single crystals. More importantly, this Mg assisted flux growth technique might open a route for the availability of most of R_2T_{17} single crystals which are surprisingly rare so far e.g. Sm_2Fe_{17}.[6]

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Crystal growth and structural characterization

$Sm_9Co_{67}Mg_{24}$ composition was loaded in a 3-capped Ta crucible[7] and growth profile similar to $Ce_{3-x}Mg_xCo_9$[8] was used for the crystal growth. The single crystals were separated from the flux at 1150°C after cooling the ampoule from 1200 °C over 99 h.

As grown Sm_2Co_{17} single crystals are presented in Figure 1(a). The plate like Sm_2Co_{17} crystals have [001] axis perpendicular to

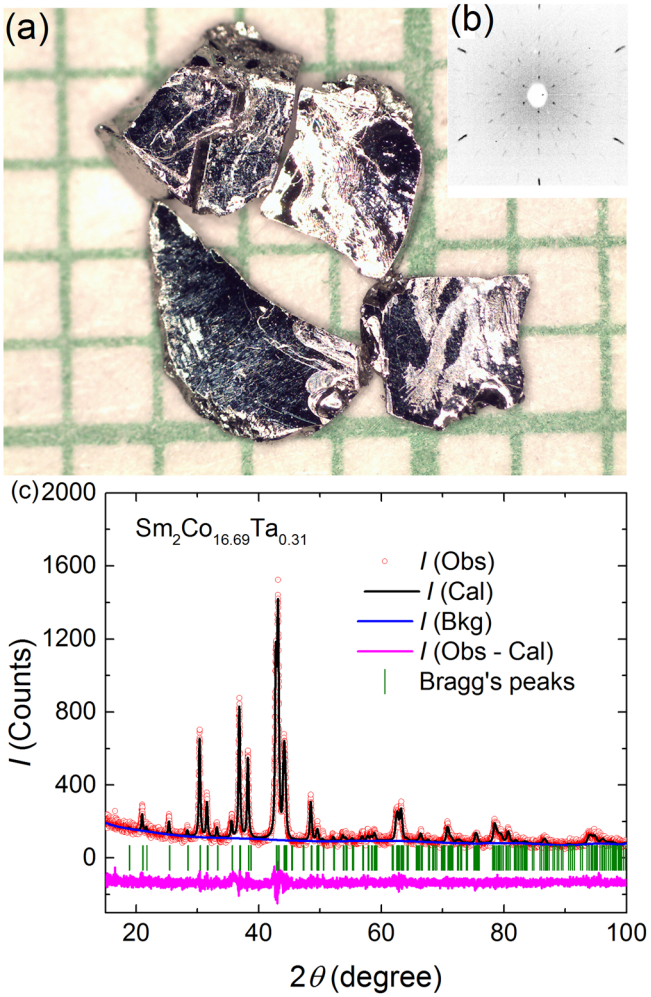

FIG. 1. (a) $Sm_2Co_{16.69}Ta_{0.31}$ single crystals over the millimeter grid (b) Laue pattern with beam direction [001]. Although the crystals are not looking xexagonal, the back-scattered Laue photograph is hexagonal. (c) Rietveld refined powder XRD for $Sm_2Co_{16.69}Ta_{0.31}$. *I*(Obs), *I*(Cal), *I*(Bkg) and *I*(Obs - Cal) are experimental, calculated, fitted background and differential diffractrogram data respectively. The vertical lines represents the various diffraction Bragg peaks.

plate as illustrated by backscattered Laue photograph with a hexagonal pattern as shown in Figure 1(b).

Initially, Sm_2Co_{17} single crystals were characterized using crushed single crystal powder x-ray diffraction (XRD) technique. These data were collected using Rigaku Miniflex II diffractormeter (Cu-K_α radiation). Finely ground Sm_2Co_{17} powder was spread over the silicon wafer sample holder with help of Dow Corning high vacuum grease and diffraction data were collected over 2θ range of 10° to 100° with a scan step of 0.01° with a dwelling time of 5 sec. Powder data were Rietveld refined using EXPGUI and GSAS software package.[9] The Rietveld refined powder XRD pattern using Th_2Zn_{17} type structure with space group *R*-3m is presented in Figure 1(c) with $R_p = 0.08$.

Then the as grown single crystals of Sm_2Co_{17} were characterized using Scanning Electron Microscopy (SEM) technique. As grown crystals were mounted in a SEM sample-mounting-epoxy both parallel and perpendicular to the plate to access both planar and cross sectional area of samples and finely polished to obtain the smooth surfaces as shown in Fig. 2. Figure 2(a) and (b) show the fine polished more or less homogeneous composition both in planar and cross sectional back scattered SEM images of Sm_2Co_{17} samples. Interestingly, even though the backscattered images looks uniform, the Energy Dispersive X-ray Spectroscopy (EDS) spectra showed small presence of Mg and Ta in the sample with a average composition of $Sm_2Co_{16.69}Ta_{0.31}$.

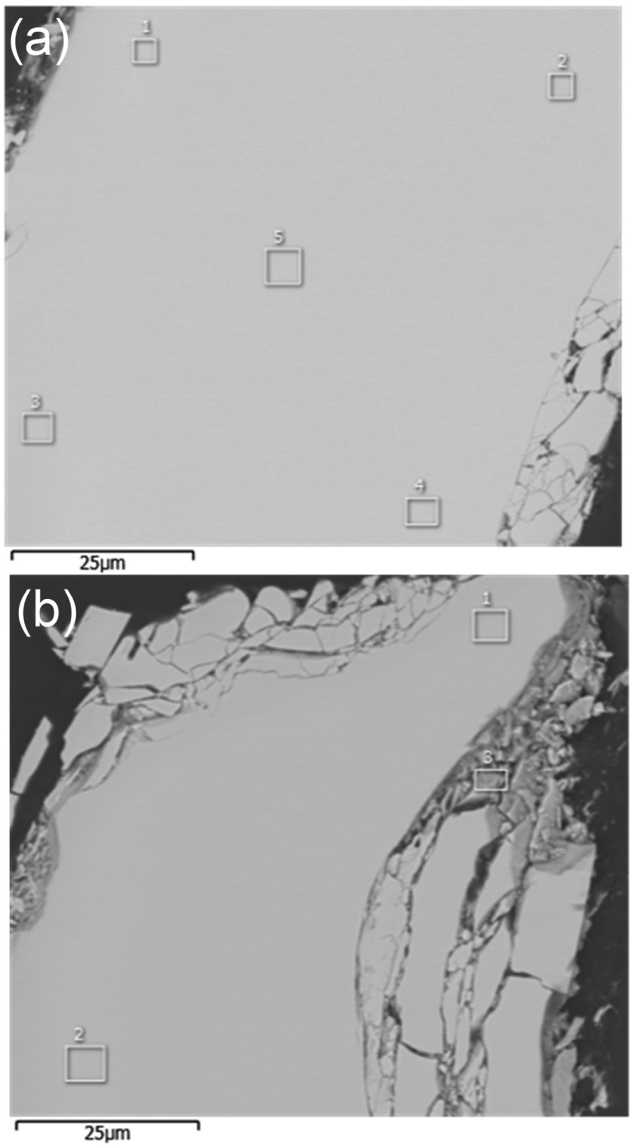

FIG. 2. (a) SEM image of as grown $Sm_2Co_{16.69}Ta_{0.31}$ single crystal along the planar view (b) along the cross section.

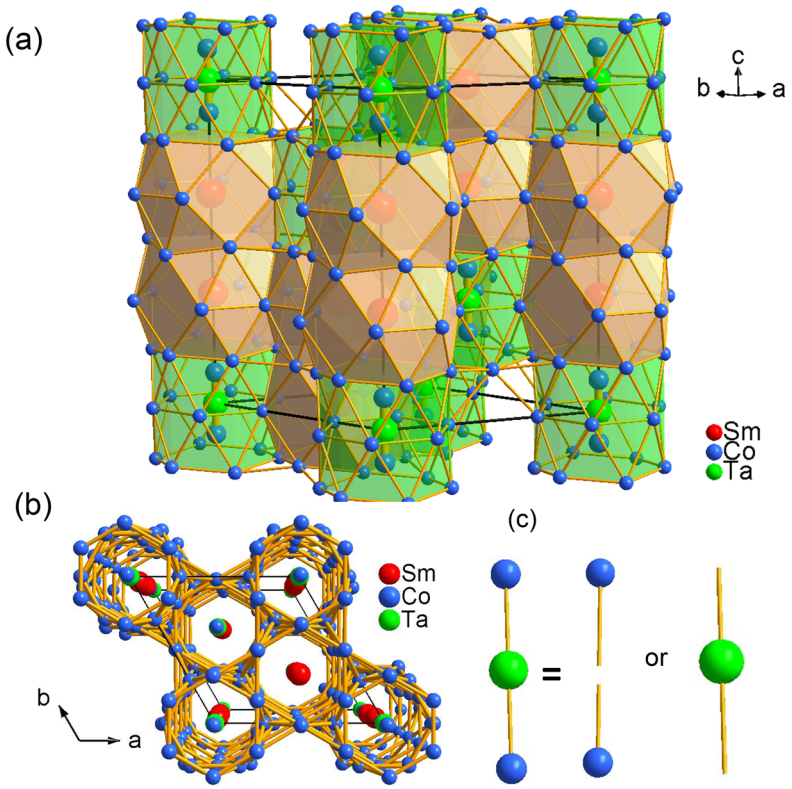

FIG. 3. (a) Crystal structure of $Sm_2Co_{16.69}Ta_{0.31}$. The Ta atoms are statistically occupying the center of Co-Co dumbbell along the specific veritcal channel. (b) Crystal structure of $Sm_2Co_{16.69}Ta_{0.31}$ viewed along the *c*-axis to demonstrate the dumbbells and Sm atoms channel. (c) Illustration of statistical replacement of Co-Co dumbbell by Ta atom.

Then we got motivated to know the specific structural site of Mg and Ta in the structure and employed a single crystalline XRD analysis.

Single crystal XRD intensity data for an as grown single crystal were collected using Bruker smart Apex-II diffractometer ($MoK_\alpha\lambda$ = 0.71073 Å) and analysed using SHELXTL structure solution software. In total, 5665 reflections were collected using 0.05° scans in ω. The average exposure time was 10 sec and the crystal to detector distance was 60 mm. In the structure solution, Mg could be included in the specific Co site but the composition is never higher than error bar. Then we dropped Mg in the composition formula. Ta atoms were found to substitute the center of Co-Co dumbbell as shown in Fig. 3(a). The structure of $Sm_2Co_{16.69}Ta_{0.31}$ (*R*-3*m*) features parallel hexagonal tunnels (defined by Co2-Co4 atoms) running along the c axis, cf. Figure 3(b). The tunnels are alternately filled by Co1-Co1 dimers and Sm atoms. In the present structure, Ta is statistically substituted for Co-Co dumbbell with Ta position being at the center of Co-Co dumbbell as shown in Figure 3(c), consistent with Zr atom position in Zr doped Sm_2Co_{17} magnet alloy predicted via lattice relaxation calculation,[10] with a refined occupancy of 2.6(2)%.

Refined crystallographic information data and conditions are presented in Table I and II below.

B. Determination of Curie temperature

Temperature and field dependent magnetization data were obtained along easy axis of $Sm_2Co_{16.69}Ta_{0.31}$ single crystals using Quantum Design vibrating sample magnetometer (VSM: 300 K - 1000 K). The Curie temperature of Sm_2Co_{17} single crystalline sample is reported to fall in between 1080 K to 1180 K window.[11–13] Getting the Curie tail of $Sm_2Co_{16.69}Ta_{0.31}$ to estimate

TABLE I. Crystal data and structure refinement for $Sm_2Co_{16.69}Ta_{0.31}$.

Empirical formula	$Sm_2Co_{16.69}Ta_{0.31}$
Formula weight	1306.99
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, *R*-3*m*
Unit cell dimensions	a=8.4075(17) Å
	c = 12.241(3) Å
Volume	749.4(3) 10^3 Å^3
Z, Calculated density	3, 8.688 g/cm^3
Absorption coefficient	39.095 mm^{-1}
Reflections collected	5665
Independent reflections	477 [R(int) = 0.0495]
Completeness to θ = 25.242°	100.00%
Absorption correction	multi-scan, empirical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	152/0/17
Goodness-of-fit on F^2	0.936
Final R indices [I > 2σ(I)]	*R*1 = 0.0216, *wR*2 = 0.0466
R indices (all data)	*R*1 = 0.0231, *wR*2 = 0.0299
Extinction coefficient	0.00188(13)
Largest diff. peak and hole	2.393 and -1.686 e.Å^{-3}

TABLE II. Atomic coordinates and equivalent isotropic displacement parameters (A^2) for $Sm_2Co_{16.69}Ta_{0.31}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	Wyck. Occ.	Symm.	x	y	z	U_{eq}
Sm	6c(1)	3m	0.0	0.0	0.3452(1)	0.005(1)
Co1	6c(0.97)	3m	0.0000	0.0000	0.0969(1)	0.006(1)
Co2	18f(1)	.2	0.2904(1)	0.0000	0	0.007(1)
Co3	9d(1)	.2/m	0.5000	0.0000	0.5000	0.006(1)
Co4	18h(1)	.m	0.5015	0.4985	0.1539	0.007(1)
Ta	3a 0.03(2)	-3m	0	0	0	0.007(2)

the transition temperature is not possible in commercially available magnetometers like QD VSM with oven option. In order to estimate the Curie temperature we used the method of generalized Bloch fitting of spontaneous magnetization data. Spontaneous magnetization data were obtained via the Y-intercept of linear fit of saturation magnetization part of M(H) data at various temperatures as shown in Fig. 4 for 300 K. The two tiny triangular vortexes in the *M(H)* loop might be the signature of ferrimagnetic coupling between Sm and Co demonstrated by domain wall movement at high field.[14,15] Such spontaneous magnetization data were taken up to 1000 K for each interval of 50 K starting from the room temperature. To reduce the uncertainty, spontaneous magnetization data were measured using a well-polished sample which could be better aligned along the easy axis during the measurements. The generalized Bloch Law was fitted as $\frac{M_S(T)}{M_S(2\ K)} = (1 - (\frac{T}{T_C})^{\alpha})^{\beta}$ shown in the inset of Figure 4 and the Curie temperature is inferred to be 1100 K.[16,17] Here $M_S(2K)$ and $M_S(T)$ are the base temperature and high temperature spontaneous magnetization data and T_C is the Curie temperature. The fitted value of the α and β are found to be 2.53 ± 0.07 and 0.49 ± 0.02 respectively.

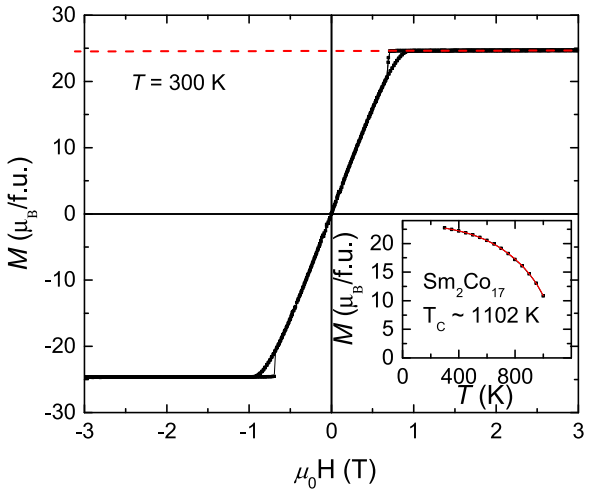

FIG. 4. Determination of the spontaneous magnetization of $Sm_2Co_{16.99}Mg_{0.01}Ta_{0.35}$ using [001] magnetization data at 300 K. See the text for a possible reason of tiny vortexes in the *M(H)* loop.

III. CONCLUSIONS

Single crystalline Sm_2Co_{17} samples were prepared using Mg assisted self-flux growth technique in a 3-caped Ta crucible. In case of Sm_2Co_{17}, Ta is found to be statistically distributed in the center of Co-Co dumbbell with an empirical formula $Sm_2Co_{16.69}Ta_{0.31}$. The Curie temperature of $Sm_2Co_{16.69}Ta_{0.31}$ is determined to be ~ 1100 K using the generalized Bloch law method.

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